*Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.*

1. (15 points) a) Two-dimensional self-assembly of organic materials can be conducted at cryogenic temperatures to build an array of useful nanostructures. However, to optimize the process, the diffusion coefficients of organic materials on flat surfaces must be known. Use a 2-D diffusion model to estimate the diffusion coefficient of a C_{60} molecule ("buckyball") on a single crystalline surface of gold in an experiment conducted at T = 50 K. Under these conditions, on average, a single buckyball moves approximately 55 nm in 10 seconds.

$$r_{rms} = \sqrt{4Dt}$$

$$D = \frac{r_{rms}^2}{4t} = \frac{(55 \times 10^{-9} m)^2}{4 \times 10\ sec} = 7.56 \times 10^{-17} \frac{m^2}{sec}$$

b) The two-dimensional diffusion coefficient is much smaller than the diffusion coefficient for the same compound dissolved in liquid benzene. Kato, Kikuchi, and Achiba (*J. Phys. Chem*. 1993, *97*, 10251-10253), using NMR measurements at room temperature, report the diffusion coefficient in a benzene solution to be:

$$D_{self} = 8.3 \times 10^{-10} \frac{m^2}{sec}$$

Use this diffusion coefficient to estimate the time needed for a C_{60} molecule at these conditions to sample the entire NMR tube. You may assume that the tube has an inch (2.54 cm) of solution.

$$This\ is\ a\ 3D\ case{:}\ r_{rms} = \sqrt{6Dt};$$

$$t = \frac{r_{rms}^2}{6D} = \frac{(0.0254\ m)^2}{6 \times 8.3 \times 10^{-10}\frac{m^2}{sec}} = 129550\ s = 36.0\ hours$$

DO NOT WRITE IN THIS SPACE
p. 1_____/15
p. 2_____/10
p. 3_____/10
p. 4_____/15
p. 5_____/10
p. 6_____/15
p. 7_____/15
p. 8_____/10
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p. 9 _____/5 (Extra credit)
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TOTAL PTS
/100

2. (10 points) A 2-cm diameter spherical ball made of stainless steel type 304 (density = 7.90 g/cm³) is dropped at 25°C through glycerol (viscosity = 10690 millipoise; density = 1.2613 g/cm³). What is the expected terminal velocity of the ball?

Answer:

$$v_{terminal} = \frac{2r^2(\rho - \rho_0)g}{9\eta} = \frac{2(1\ cm)^2(7.90 - 1.2613)\left(\frac{g}{cm^3}\right)980\frac{cm}{s^2}}{9 \times \left(10.69\frac{g}{cm \times s}\right)} = 135.2\frac{cm}{s} = 1.352\frac{m}{s}$$

Score for Page

3. (10 points) From the statements in column B, select the best match for each phrase in column A and put its letter in the adjacent blank. There is only one best match for each phrase.

Column A	Column B
1. According to the kinetic theory of gases, the average speed of gas molecules is always ___m___ than their RMS speed. 2. In the expression of viscous force, the coefficient η is referred to as ___i___. 3. The Stokes-Einstein equation describes diffusion of a ___k___ object. 4. If a sedimentation process is performed using centrifugal acceleration instead of gravity acceleration (on the order of 10^5 acceleration of gravity), such a process is called ___e___. 5. Poiseuille's law describes ___h___	a) cubic b) cooler c) flow of a liquid through a round tube under conditions of turbulent flow d) sedimentation coefficient e) ultracentrifugation f) larger g) elongated h) flow of a liquid through a round tube under conditions of laminar flow i) viscosity j) nicer k) spherical l) saturation centrifugation m) smaller n) ultracenturation o) density coefficient p) the journey of Hercules on his way home q) coefficient of viscous force r) the end of the world

Score for Page

4. (15 points) Air is a mixture. Neglecting tiny amounts of other gases, air can be considered to be 78 mole % N_2 and 22 mole % O_2. What is the total number of N_2-O_2 collisions per second in one cm^3 of air at a total pressure of exactly one bar and 298.15 K? [HINT: To make this calculation, you will need to know the "size" of nitrogen and oxygen molecules. The diameter of the N_2 molecule is reported to be 364 pm, and the diameter of the O_2 molecule is reported to be 346 pm.]

The total collision frequency in a binary mixture is determined by the equation

$$Z_{AB} \quad = \quad \sigma_{AB} <v>_{AB} \, n_A^* n_B^*$$

The collision cross-section is given by

$$\sigma_{AB} \quad = \quad \pi(r_A + r_B)^2 \quad = \quad \pi\left(\frac{3.64 \times 10^{-10} m}{2} + \frac{3.46 \times 10^{-10} m}{2}\right)^2 \quad = \quad 3.9592 \times 10^{-19} \, m^2$$

The relative velocity is calculated by

$$<v_{AB}> \quad = \quad \sqrt{\frac{8kT}{\pi\mu}}$$

The reduced mass is calculated from the masses of the two materials. On a molar basis, it is

$$\mu_{molar} \quad = \quad \frac{M_{nitrogen} M_{oxygen}}{M_{nitrogen} + M_{oxygen}} \quad = \quad \frac{2 \times 14.0067g \times 2 \times 15.9994g}{2(14.0067 + 15.9994)g} \quad = \quad 14.93688 \, g \, mole^{-1}$$

We can calculate per molecule, or we can calculate on a molar basis, using R instead of k. They both give the same result, so we choose the latter.

$$<v_{AB}> \quad = \quad \sqrt{\frac{8RT}{\pi\mu_{molar}}} \quad = \quad \sqrt{\frac{8(8.3144349 \, J \, K^{-1} mole^{-1})(298.15 \, K)}{\pi(0.01493688 \, kg \, mole^{-1})}} \quad = \quad 650.09 \, m \, s^{-1}$$

The number densities are calculated from the partial pressures.

$$n_i^* \quad = \quad \frac{P_i N_0}{RT}$$

For example, for nitrogen

$$n_{nitrogen}^* \quad = \quad \frac{P_{nitrogen} N_0}{RT} \quad = \quad \frac{0.78 \times 10^5 Pa(6.02211415 \times 10^{23} \, mole^{-1})}{8.3144349 \, J \, K^{-1} \, mole^{-1}(298.15 \, K)} \quad = \quad 1.8949 \times 10^{25} \, m^{-3}$$

Similarly one can do a similar calculation of the number density of oxygen in air:

$$n_{oxygen}^* \quad = \quad \frac{P_{oxygen} N_0}{RT} \quad = \quad \frac{0.22 \times 10^5 Pa(6.02211415 \times 10^{23} \, mole^{-1})}{8.3144349 \, J \, K^{-1} \, mole^{-1}(298.15 \, K)} \quad = \quad 5.3444 \times 10^{24} \, m^{-3}$$

Putting all of these together gives total collision frequency per volume:

$$Z_{AB} \quad = \quad \sigma_{AB} <v>_{AB} \, n_A^* n_B^* \quad = \quad (3.9592 \times 10^{-19} m^2)(650.09 \, m \, s^{-1})(1.8949 \times 10^{25} \, m^{-3})(5.3444 \times 10^{24} \, m^{-3})$$
$$= \quad 2.606 \times 10^{34} \, m^{-3} \, s^{-1}$$

In a volume of 1 cm^3, the number of collisions is

$Number \, of \, collisions \, = \, Z_{AB} \, (volume) \, = \, 2.606 \times 10^{34} \, m^{-3} \, s^{-1} \, (10^{-6} \, m^3) \quad = \quad 2.606 \times 10^{28} \, s^{-1}$

Score for Page

5. (10 points) Bishop and Engel (*J. Amer. Chem. Soc.* **1975**, *97*, 6754 – 6762) studied the temperature dependence of the decomposition of the *cis*-azoalkane shown at the right. The temperature-dependent rate constants they reported are shown in the table as a function of temperature.
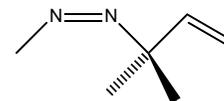
T (°C)	-24.82	-20.73	-17.02	-13.00	-8.95
k_1 (s^{-1})	1.22×10^{-4}	2.31×10^{-4}	4.39×10^{-4}	8.50×10^{-4}	1.43×10^{-3}

Using all of these data, determine the enthalpy of activation, $\Delta H^{\ddagger}$. (You <u>must</u> show a proper plot that explains how you found this enthalpy of activation.)

One plots the natural logarithm of the rate constant divided by the absolute temperature (in kelvins) versus the inverse of the absolute temperature.

$\ln(k/T) = -10121/T + 26.167$
$R^2 = 0.9985$
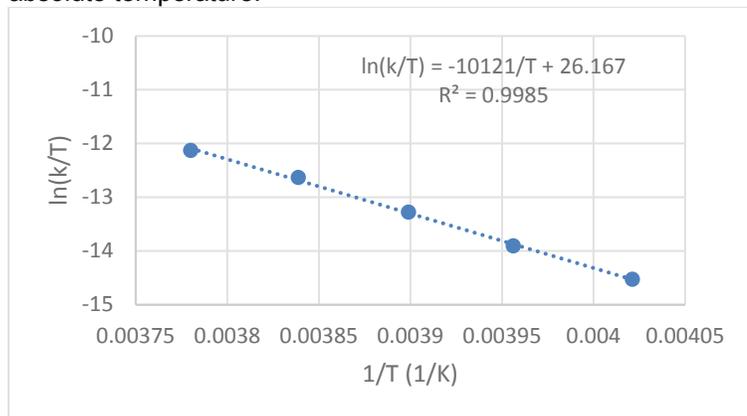
From the slope, one finds the enthalpy of activation:

$$\Delta H^{\ddagger} = -slope\,(R) = (10121\ K)\left(8.3144349\,\frac{J}{K-mol}\right) = 84.1\ kJ/mol$$

Score for Page

6. (15 points) Hydrogen iodide can be synthesized from the elements in a gas-phase reaction. One proposed mechanism for the process is

$$I_2 \quad \rightarrow \quad 2\,I \qquad v_1 \;=\; k_1[I_2]$$
$$2\,I \quad \rightarrow \quad I_2 \qquad v_2 \;=\; k_2\,[I]^2$$
$$H_2 + 2\,I \rightarrow 2\,HI \qquad v_3 \;=\; k_3[H_2][I]^2$$
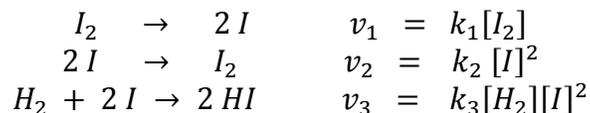
Derive a differential rate law for the rate of production of HI if:
a) I_2 and I are in a fast equilibrium throughout the reaction.

$$K_{eq} \;=\; \frac{[I]^2}{[I_2]}$$

Therefore $[I]^2 \;=\; K_{eq}[I_2]$

The rate of production of HI is given by:

$$\frac{d[HI]}{dt} \;=\; 2\,v_3 \;=\; 2k_3[H_2][I]^2 \;=\; 2\,k_3 K_{eq}[H_2][I_2] \;=\; 2\,\frac{k_3 k_1}{k_2}[H_2][I_2]$$

b) the steady-state approximation can be applied to the I atoms.

In this case, one starts with

$$\frac{d[I]}{dt} \;=\; 2v_1 \;-\; 2v_2 \;-\; 2v_3 \;=\; 0$$

By substitution

$$\frac{d[I]}{dt} \;=\; 0 \;=\; 2k_1[I_2] \;-\; 2k_2[I]^2 \;-\; 2k_3[H_2][I]^2$$

This equation gives the steady-state value of the atom concentration:

$$[I]^2 \;=\; \frac{k_1[I_2]}{k_2 + k_3[H_2]}$$

Under these conditions, the rate of production of HI is:

$$\frac{d[HI]}{dt} \;=\; 2\,v_3 \;=\; 2\,k_3[H_2][I]^2 \;=\; \frac{2k_3 k_1[H_2][I_2]}{k_2 + k_3[H_2]}$$

Note the similarities between this result and the previous one. Also note the differences between these two approximations.

Score for Page

7. (15 points) The adsorption of a particular gas, A, is described well by the Langmuir isotherm with the Langmuir constant b_A = 0.85 kPa^{-1} at 25°C. (a) Calculate the pressure at which the fractional coverage is 0.15.

$$\Theta \;\; = \;\; \frac{b_A P_A}{1 + b_A P_A}$$

By rearrangement of this formula, one obtains an expression for the pressure in terms of the fractional coverage.

$$P_A \;\; = \;\; \frac{\Theta}{b_A(1 - \Theta)} \;\; = \;\; \frac{0.15}{0.85 kPa^{-1}(1 - 0.15)} \;\; = \;\; 0.208 \; kPa$$

(b) Suppose one has a surface that is in equilibrium with two gases, one with b_A = 0.85 kPa^{-1} and another with b_B = 1.7 kPa^{-1} at 25°C. Calculate the <u>total pressure</u> of a 50:50 mixture of these gases at which the fractional coverage of gas A is 0.15.

$$\Theta_A \;\; = \;\; \frac{b_A P_A}{1 + b_A P_A + b_B P_B}, \qquad but \quad P_A \;\; = \;\; P_B$$

The equality of the two gas pressures means one only has to find the partial pressure of one gas, call it P_A.

$$0.15 \;\; = \;\; \frac{b_A P_A}{1 + b_A P_A + b_B P_A} \;\; = \;\; \frac{b_A P_A}{1 + (b_A + b_B)P_A}$$

The equation can be rearranged to allow one to find the partial pressure, P_A.

$$0.15 \;\; = \;\; b_A P_A - 0.15(b_A + b_B)P_A \;\; = \;\; (0.85 b_A - 0.15 b_B)P_A$$

And this equation can be rearranged to:

$$P_A \;\; = \;\; \frac{0.15}{0.85 b_A - 0.15 b_B} \;\; = \;\; \frac{0.15}{0.85(0.85 kPa^{-1}) - 0.15(1.7 kPa^{-1})} \;\; = \;\; 0.32 \; kPa$$

The question asked for the total pressure. Because the two partial pressures are equal, one may easily find the total pressure as double the partial pressure of component A.

$$P_{total} \;\; = \;\; P_A + P_B \;\; = \;\; 2 P_A \;\; = \;\; 0.64 \; kPa$$

Score for Page

8. (10 points) Fill in each blank with a single word or symbol.

a) In the equation describing reaction rate, the rate of change of the reactant concentration is _____*negative*_____.

b) In simple collision theory, the coefficient *p* in the bimolecular rate constant is always _____*less*_____ than 1.

c) In the Langmuir adsorption model, the equilibrium coverage of a component A _____*decreases*_____ when a second component is present in the gas phase.

d) In Michaelis-Menten kinetics describing enzyme catalysis, the meaning of _____K_m_____ is the concentration of the substrate at half of the maximum initial reaction rate.

e) A radioactive decay is a classic example of _____*first*_____ order process.

Score for Page

9. (5 points, extra credit) In class, we talked about the mechanism of the formation of hydrogen bromide from its elements:

$$H_2 \ (g) + \ Br_2 \ (g) \quad \rightarrow \quad 2 \ HBr \ (g)$$
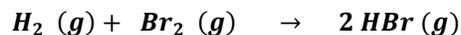
One proposed mechanism of this reaction gives the following prediction of the rate law:

$$Rate \quad = \quad \left(\frac{k_1 k_2^2 k_3^2}{k_5} \right)^{1/2} \frac{[H_2][Br_2]^{3/2}}{k_3[Br_2] + \ k_4 \ [HBr]}$$

where the various k's are rate constants for various elementary steps. Consider the overall reaction.

(a) What is the apparent initial order with respect to Br₂ for this reaction?

Apparent initial order with respect to Br₂ is ½.

(b) What is the apparent initial order with respect to HBr?

Apparent initial order with respect to HBr is 0.

(c) What is the initial order with respect to hydrogen?

The order with respect to H₂ is always 1.

(d) What is the apparent order with respect to HBr near the end of reaction?

The apparent order with respect to HBr as the concentration builds up is -1.

Score for Page